



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
Docket No. 12329US03

In the Application of:

ROGER BERNARDS, HECTOR
GONZALEZ, AL KUCERA and
MIKE SCHANHAAR

U.S. Serial No.: 10/028,955

Filed: December 18, 2001

For: METHOD FOR ROUGHENING
COPPER SURFACES FOR
BONDING TO SUBSTRATES

Examiner: S. Ahmed

Group Art Unit: 1765

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail, postage prepaid, in an envelope addressed to: Mail Stop Amendments, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on May 2, 2005. Express Mail Label No. EV-639807253 US

By: _____

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DECLARATION UNDER 37 C.F.R. § 1.131

Commissioner for Patents
P.O. Box 1450
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Sir:

We, Roger Bernards, Hector Gonzalez, Al Kucera, and Mike Schanhaar, declare the following:

1. We are the applicants of the above-identified patent application and coinventors of the subject matter described and claimed therein.
2. Prior to the effective filing date of United States Patent No. 6,106,899 ("Nakagawa"), which is July 16, 1998, we reduced to practice the idea of a process for preparing roughened copper surfaces comprising the steps of contacting with a clean copper surface an adhesion promoting composition under conditions effective to provide

a roughened copper surface, wherein the adhesion promoting composition consists essentially of hydrogen peroxide, a pH adjuster, a topography modifier, and a uniformity enhancer, and at least essentially free of halogen ions.

3. Prior to the effective filing date of Nakagawa, we completed our invention as described and claimed in at least claim 1 of the present application, as evidenced by the laboratory notebook pages attached as Exhibit A.

4. The laboratory notebook pages are those of one of the undersigned applicants, Roger Bernards.

5. The first page (laboratory notebook page 29) describes the commencement of a multi-day experiment designed to develop a process for preparing roughened copper surfaces.

6. As shown on this page, a standard bath was used for each set of runs in the experiment. The standard bath contained:

- (a) H_2O_2 (hydrogen peroxide),
- (b) H_2SO_4 (sulfuric acid), and
- (c) CuSO_4 (copper sulfate).

7. The run "sets" that follow on the first and subsequent pages describe additional components that were added to the standard bath prior to applying the composition to a copper surface.

8. Set "K" is described on page 34. The heading for Set K indicates the component that was added to the standard bath for this set of runs: "5 Amino Tetrazole • H_2O ".

9. Set K consists of 13 runs. Each run lists the concentration of 5-aminotetrazole added to the standard bath, plus any additional components that were added. Run 4 lists: ".5 g/L + 1.5 g/L BTA". BTA is an acronym for benzotriazole. In run 4, therefore, 0.5 g/L of 5-aminotetrazole and 1.5 g/L of benzotriazole were added to the standard bath.

10. Thus, the composition used in Run 4 of Set K contained the following components:


- (a) hydrogen peroxide,
- (b) a pH adjuster (sulfuric acid),
- (c) a topography modifier (benzotriazole),
- (d) a uniformity enhancer (5-aminotetrazole), and
- (e) copper sulfate.

11. As explained on laboratory notebook page 34, the composition of Run 4 was successful when applied to a copper surface: "Dark and very uniform looks great" and "What's awesome about #4 and #9 and others on this page is that no matter how [expletive] the surface is before going into the etch you get complete coverage with no skip etch."

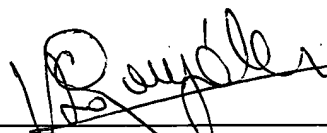
12. Each of the dates deleted from Exhibit A is prior to the effective filing date of Nakagawa.

13. We certify that all statements made herein of our own knowledge are true, and that all statements made herein on information and belief are believed to be true. We understand that willful false statements and the like are punishable by fine or


imprisonment, or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.


Roger Bernards

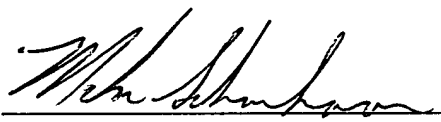
4/22/05
Date


Hector Gonzalez

4/22/05
Date


Al Kucera

4/22/05
Date


Mike Schanhaar

4/22/05
Date

objective To make a dark coating with Cobra band + additives other than BTA

Standard Bath: H_2O_2 : 3% Temp 98°F (from 5% H_2SO_4 add)
 H_2SO_4 : 5% 94°F - 97°F
 $CuSO_4 \cdot 5H_2O$: 40 g/L
 Cl^- : Zero unless listed
 Additive: Variable

3-X Set A: Cobratec 928 — Material (only 90% active (not taken into account 50 g/L))

		Gross	Tare	Dwell (min)	Etch	Appearance
(1)	1 g/L	1.5870	1.5159	1:10	80.5	Slightly darkened
(2)	3 g/L	1.5916	1.5326	1	67	Lighter but cool looking
(3)	5 g/L	1.5671	1.5165	1	57	same
(4)	7 g/L	1.5607	1.5148	1	52	same
(5)	10 g/L	1.5372	1.4891	1	54	same
(6)	15 g/L	1.6355	1.5866	1	55	maybe not as rough
(7)	25 g/L	1.6315	1.5857	1	52	maybe not as rough
(8)	0.5 g/L	1.5764	1.5172	1	67	not as rough looking

3-X SET B Cobratec PT (The PT Solution has 10% H_2SO_4)

(1)	10 g/L	1.5997	1.5328	1	76	looks very smooth
(2)	1 g/L (active material)	1.5956	1.5520	1	49	Striations on top side Bottom side looks not etched
(3)	2 g/L					
(4)	2 g/L Repeat	1.6062	1.5338	1:20	82	Striations
(5)	2 g/L + 5 g/L Cl^-	1.6068	1.5995	1:20	8.3	No etch
(6)	3 g/L	1.5963	1.5225	1:20	84	Striations Big time
(7)	4 g/L	?	1.5388	1:28	80	Striations
(8)	4 g/L	1.5921	1.5288	1:20	72	"
(9)	5 g/L	1.6065	1.5355	1:20	80	"
(10)	7 g/L	1.5990	1.4924	1:20	121	"
(11)	10 g/L	1.5701	1.5211	1:00	55	"
(12)	15 g/L adjusted for H_2SO_4	1.5791	1.4745	1:50	118	"
(13)	1.5 g/L	1.6021	1.5227	1:20	90	Nonuniform thin marker
(14)	2.5	1.5961	1.5071	1:20	101	Striations Fat marker

Cont. pg 30

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SIGNATURE

Zee Burger

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RB

From pg 29

10.01

3 X Set C

TT 100 (Cobrotest TT100)

	Gross	Tare	Total Etch	Dwell
1) 0g/L	1.5813	1.4838	110	1:25
2) 1g/L 36% H_2O_2	1.5981	1.5061	104	1:20
3) 1g/L	1.5982	1.4978	114	1:20
4) 2g/L	1.5988	1.5112	91	1:20
5) 3g/L	1.5958	1.5083	99	1:20
6) 4g/L	1.5915	1.4560	108	1:23
7) 6g/L	1.5454	1.4644	92	1:20
8) 10g/L	1.5770			

Appearance
dull copper

6 X Set D Alpha prep PC 70827042

1) 50% + 3% H_2O_2	1.5907	1.5660	28	1:20	look oxidized
2) " + 6% H_2O_2	1.5787	1.5352	49	1:20	striations
3) " + 9% H_2O_2	1.6033	1.5281	85	1:20	BTA on surface
4) " + 9% H_2O_2 + 4.3.9% H_2SO_4 (5% total)	1.5909	1.5025	100	1:20	striations
5) " + 9% H_2O_2 + 3.9% H_2SO_4 + 13.5g/L $CuSO_4 \cdot 5H_2O$	1.5770	1.4993	38	1:30	Bath turned green

6 X SET E NaBr at 8.5g/L BTA

1) 1.4g/L 3% H_2O_2	1.5857	1.5776		1:20
2) " 6% H_2O_2	1.5956	1.5843	13	1:20
3) " 9% H_2O_2	1.6040	1.5852	21	1:20
4) " + 12% H_2O_2	1.5867	1.4727	129	1:20
5) 1.2g/L 14% H_2O_2	1.5826 1.5735 1.6149	1.5348	91	1:20

Looks like Cobra with et

Looks Like Cobra w. Cl⁻ stained

Cont. on pg 32

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Lee B. Binger

RIB

6) 0.53 g/L NaBr 1.5739 1.5138 68 1120 Stained like et
 + 14% H_2O_2
 + 8.53 g/L BTA

~~Glicat F-1 1.5879 1.5878~~
~~+ 5% H_2SO_4~~
~~+ 3% H_2O_2~~

SET F Glicat F-1 Lot 961205 exp [REDACTED]

Normal Conditions i.e. 5% H_2SO_4 + 3% H_2O_2 + 40 g/L $CaSO_4 \cdot 5H_2O$, 98°F

25% by Vol F-1 1.5872 1.5866 0.7 1130 Bright water beads up on it

25% + 9% H_2O_2 1.6080 1.6076 still no etch "

10% + 3% H_2O_2 1.6049 1.6040

20% + 14% H_2O_2 1.6191 1.6140 6 2100 Still no etch

2% + 3% H_2O_2 1.5761 1.5698 7 1120

2% + 14% H_2O_2 1.5752 1.5443 35 1120 Still Bright but not as shiny

Part gasses like ~~crack~~
 but still hardly no etch
 H_2O_2 Breaking down by
 side Rx

6X → SET G Glicat E2L

2% + 3% H_2O_2 1.5728 1.5446 32 1120 Bright but not shiny

2% + 6% H_2O_2 1.6035 1.5034 112 2200 Bright but not shiny

Part really gassing no not much etch

Conti pg 33

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2x SET H 1- Methylimidazole normal conditions unless otherwise stated

- (1) Sg/L 1.5998 1.5803 22 1:20 Bright Shiny
- (2) Sg/L + 8.5 BTA 1.5797 1.5150 73 1:20 not as Dark as jvs + BTA
- (3) , Sg/L + ~~8.5 BTA~~
+ 3.0 BTA
_{2A} 1.5056 fairly Dark

3X SET I 2, 1, 3 Benzo thiadiazole

- (1) 5g/L 1.6117 1.5537 66 1:30 Light
Not all dissolved looks completely insoluble
- (2) 5g/L + 3g/L BTA 1.5755 1.5043 81 4:20 Slightly Dark

3X SET J 1H-2,1,2,3 Triazole (4,5-b) pyridine

- | | | | | | |
|--------------------------------|-------------------|-------------------|----|------|--|
| 1) 5g/L | 1.5982 | 1.5435 | 62 | 1:20 | Big Time striations
Looks like fire |
| 2) 5g/L + 3g/L BTA | 1.5900 | 1.5296 | 68 | 1:20 | Brown |
| 3) 10g/L | 1.5983 | 1.5385 | 68 | 1:20 | striations Bad |
| 4) 10g/L + 3g/L BTA | 1.5535 | 1.5383 | | 1:20 | Still some striations |
| 5) 5g/L | 1.5972 | 1.5169 | 91 | 1:20 | Striations |
| 6) 5g/L + 3g/L BTA | 1.5748 | 1.4955 | 90 | 1:25 | Looks like BTA only
Marker spreads |

Cont. on Pg 34

2 X SET K

5 Amino Tetrazole H₂O.

- 1) 5g/L 1.5839 1.5313 60 1:20 Light but rough
- 2) 5g/L + 3g/L BTA 1.5744 1.5096 73 1:35 Reddish Looking Marker spreads
- 3) 0.5g/L — 1:20 Looks like BTA Little lighter
- 4) .5g/L + 1.5g/L BTA 1.4935 1.3685 142 1:50 Dark and very uniform looks great
- 5) .5g/L + 3g/L BTA ~~1.4979~~ ~~1.4879~~ 1:20 Darker put not uniform skip
- 6) 0.25g/L 1.5798 Per lighter fairly uniform
- 7) .25g/L + .5g/L BTA 1.6148 1.5419 82 Lighter fairly uniform
- 8) .25g/L + 1g/L BTA 1.5892 1.5212 ~~0.68~~ 77 1:20 Kinda Dark ~~fairly uniform~~ Not uniform
- 9) .5g + .5g BTA 1.5777 1.5046 83 1:28 Dark even notes Dark as #4

and others on this page

Note: What's Awesome about #4 and #9 is that no matter how shitty the surface is before going into the etch you get complete coverage with no skip/etch

- 10) .5g/L + 1g/L BTA 1.6180 1.5552 71 1:20 Dark even, notes Dark as 4
- 11) 1g/L + 1g/L BTA 1.5845 1.5280 64 1:20 Down side is darker than up notes Dark as 10
- 12) 1g/L + 2g/L BTA 1.6051 1.5348 80 1:27 Dark uniform complete coverage
- 13) 1g/L + 3g/L BTA 1.6103 1.5432 76 1:21

Cont on pg 34

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DATE

DATE

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The main conclusion drawn from the testing of the many additives from pages 27-47 can be found on pg 34 from ~~Set K~~ ^(Set K) ~~The~~. See the note entered on that page. The 5 Amino tetrazole acts as a uniformity enhancer if it is in the right concentration and if it is in the right ratio with the BTA. This is a big improvement over the BTA only system and may be patentable. Further testing by others at electrochemicals [See Al Kucera's, Hector Gonzales' and Mike Schanhaar's Notebooks] Also show that the 5 amino tetrazole acts as a uniformity enhancer, i.e. the panels look more uniform in color, degree of etch, ^{and} coverage of the coating when the 5 amino tetrazole is used in conjunction with the BTA. Also the 5 amino tetrazole when used as the sole additive is not as uniform as when used in conjunction with the BTA. On pg-34 #4 is definitely better than #1 as ~~was~~ was noted when I said wrote #4 "looks great." The optimum Ratio of BTA to 5 amino tetrazole is close to 3 to 1 and the best concentration of BTA is close to 1.5g/L and the best concentration for 5 amino tetrazole is ^{close to} 0.5g/L. The H_2O_2 , H_2SO_4 , Temp., Copper (Copper can be zero, Copper is not needed to make this formulation work properly), Concentrations can vary a lot but I think H_2O_2 = .2% - 5%, H_2SO_4 .1% - 8%, and Temp 60°F - 130°F is the best range. Most commonly H_2O_2 = 1% - 2%, H_2SO_4 4 - 6%, and Temp 80 - 100°F is employed.

Rogn Bun

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Lee Bright

RIB